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1. Title of the Invention

METHOD FOR MANUFACTURE OF ULTRATHIN COPPER FOIL

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Specification

1. Title of the Invention

METHOD FOR MANUFACTURE OF ULTRATHIN COPPER FOIL

2. Patent Claims

A method for the manufacture of an ultrathin copper foil by conducting zinc substitution plating on the edge portion of one surface of an aluminum foil or aluminum alloy foil, then conducting copper plating to a thickness of 0.5-12 μm in a copper pyrophosphate plating bath on

the entire surface of said surface, and then conducting copper plating to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

3. Detailed Description of the Invention

The present invention relates to a method for the manufacture of an ultrathin copper foil for high-density printed circuit boards in which a wiring width and wire spacing are greatly decreased.

In recent years, significant progress in electronics technology created a demand for highly reliable high-density printed circuit boards. In particular, in the copper-clad laminates for printed circuits of computers, it became necessary to form ultrafine circuits with a wiring width and wiring spacing of no more than 0.2 mm. However, the thickness of the conventionally used copper foils was as large as about 85 μm. Therefore, in the etching technology at the time, when circuits were formed from such copper foil-clad laminates, there was a danger that the copper foils would be undercut by side etching (a lower side portion of a groove is etched on the periphery thereof and a recess-like portion is obtained), causing a short circuit. For this reason, circuits with high-density wiring widths and wiring spacing could not be obtained. Therefore, it was impossible to obtain highly reliable printed circuits with a high density.

Accordingly, thin copper foils with a thickness of 18-25 μm were used to attain this object. However, since they were manufactured by electrolytic methods similar to those for the manufacture of the above-mentioned thick copper foils, pinholes easily occurred. Moreover, because the foils were so thin, "wrinkles" and "scratches" could easily occur when the foils were handled. A low production yield and a high cost were other drawbacks associated with such ultrathin foils. Furthermore, when such copper foils were employed for forming high-density circuits by a photoresist method, the lower limit for the wiring width and wiring spacing was 0.2 mm, and high-density circuits with an ultrafine pattern having wiring widths and spacing less than this limit were difficult to produce.

An improved method was suggested, this method using an ultrathin copper foil formed by employing an aluminum foil, etc. as a pseudo-substrate and electroplating a copper layer with a thickness of no more than 18 μm thereupon. A glass-epoxy base material was laminated on the copper foil surface, the aluminum foil serving as a pseudo-substrate was removed by chemical or mechanical peeling method, and the resulting copper foil laminated sheet was used to form a high-density circuit by the aforesaid photoresist process. Such a method is disclosed, for example, in Japanese Patent Application Laid-open 48-85857.

However, with such a method, it is necessary to conduct zinc substitution plating on the electrocoating surface of the aluminum foil in advance in order to provide for good bonding strength of the ultrathin copper layer formed by electroplating with the aluminum foil serving as a pseudo-substrate and it was also necessary to dissolve and remove the aluminum and zinc chemically in order to obtain a copper clad laminate after lamination of the glass-epoxy base material. Therefore, in addition to those two types being complicated and wastewater treatment being difficult, there are disadvantages in that the copper layer is partially dissolved when the zinc is removed, and circuit shorts occur easily.

With another suggested method, copper cyanide plating is conducted on one surface of the aluminum foil of the pre-degreased and activated pseudo-substrate. However, in such a case, the copper adhesion strength is insufficient. For this reason, when in subsequent processes a thick copper plating was conducted with an acidic copper plating bath and then treatment was

conducted to increase the adhesive force, the copper layer could be easily peeled off and removed from the surface of aluminum foil. Moreover, when the thickness of the copper plating was less than 12 μm, a large number of fine pinholes were present and the product was not suitable for practical use.

The inventors have conducted an intensive study aimed at the resolution of the above-described problems. Based on the results obtained, a method was developed for the manufacture of an ultrathin copper foil designed for the formation of highly reliable printed circuits with a high density. Thus, with the method in accordance with the present invention zinc substitution plating is conducted on the edge portion on one surface of an aluminum or aluminum alloy foil (referred to simply as aluminum foil hereinbelow), then copper plating is conducted to a thickness of 0.5-12 μm in a copper pyrophosphate plating bath on the entirety of that one surface, and then copper plating is conducted to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

The method in accordance with the present invention will be described hereinbelow in greater detail.

At least one surface of an aluminum foil with a thickness of 30-70 μm (a long foil with a width of 300-1300 mm) is degreased with an alkaline cleaner and washed with water according to the usual procedure. If necessary, washing with water is conducted after pickling with 50% HNO_3 or activation.

Then an edge portion on one surface of the foil is immersed for 2-120 sec in the so-called zincate bath and zinc substitution plating is conducted. In this case, the edge portion as referred to hereinabove is a frame-like portion located on the periphery of the aluminum foil; it has a width of 2-100 mm, preferably, 10-50 mm. This width is referred to as an edge width.

The zinc substitution plating is conducted to improve adhesion of copper layer to the aluminum foil in the portions that are directly subjected to copper plating. Thus, when the end portion of the aluminum foil is not subjected to zinc substitution plating, a copper pyrophosphate plating itself cannot provide for a sufficient bonding strength with the surface of aluminum foil. When, in such a state, water washing and copper sulfate thick plating are performed in the subsequent process, the copper layer can easily peel from the edge portion of the aluminum foil. Moreover, if the coating peels off even slightly, then water or plating solution rapidly penetrates into the interface between the aluminum foil and copper layer, the surface of aluminum foil is corroded mainly by the plating solution, and the peeling is further promoted. Even if the substrates in such a state are finally dried, since the major portion of the copper layer has peeled from the pseudo-substrate, "wrinkles" or a large number of pinholes appear therein, making the foil unsuitable for practical use. However, if zinc substitution plating of the edge portion of aluminum foil is conducted as described above, the bonding strength with respect to the copper pyrophosphate plating bath is also improved and no peeling occurs in subsequent plating in a copper sulfate bath. Moreover, when the copper plating is formed to a thickness of no less than 5 μm, practically no pinholes are formed.

Immediately after completion of the zinc substitution plating, a copper layer with a thickness of 0.5-12 μm is plated by using a copper pyrophosphate plating bath, followed by washing with water. In such a case, no specific limitation is placed on the composition of the copper pyrophosphate plating bath, but it is preferred that the copper concentration be 5-100 gL, the concentration of potassium pyrophosphate be 100-500 g/L, and the pH be 8-12. As for the plating conditions, the bath temperature is within a range from normal temperature to 70°C, the electric current density is 1-5 A/dm^2, and the electrolysis time is 5-25 sec.

The copper pyrophosphate plating bath is selected for the purposes of the present invention because the coating obtained with such a bath has better adhesion to aluminum foils than that obtained with other copper plating baths, and, naturally, no peeling occurs in the lamination of laminated base materials for printed circuits. Furthermore, in addition to that fact that stronger adhesion cannot be maintained, it is not necessary to chemically dissolve and remove the aluminum foil pseudo-substrate after lamination of the base material, and peeling can be conducted by a simple mechanical means. As a result, wastewater treatment is made unnecessary, and the aluminum used can be easily recovered in the form of aluminum chips. Furthermore, a copper pyrophosphate plating bath makes it possible to conduct uniform electrocoating, and a coating can be obtained which is smooth and has good gloss. Moreover, a very small number of pinholes appear even when a thin copper foil is obtained. The thickness of the copper pyrophosphate plating is limited to 0.5-1.2 μm for the following reasons. When the thickness is less than 0.5 μm, the number of pinholes in a thin copper foil obtained increases, making it unsuitable for practical use. On the other hand, when the thickness exceeds 12 μm, since the upper limit of thickness of thin copper foils is 15 μm, the copper sulfate plating in the subsequent process cannot be conducted. Moreover, adhesion to plastic laminated base materials is degraded. The thickness of the copper foil layer is preferably 2-7 μm.

Plating copper to a thickness of 8-12 μm in a copper plating bath containing copper sulfate is conducted as a method for roughening of the copper foil layer. Appropriate conditions of such treatment should be selected and no specific limitation is placed thereon. Typically the copper plating bath has a copper concentration of 20-60 g/L and a sulfuric acid concentration of 40-150 g/L. The bath temperature is preferably within a range from normal temperature to 60°C. As for the electric current density and electrolysis time, they are somewhat affected on the liquid flow parameters, stirring state, and plating thickness, but preferably they are usually within the ranges of 5-40 A/dm^2 and 1-10 min, respectively. The external appearance of the obtained copper plated film must be such that velvety peaks and valleys of red color are formed.

The thickness of the copper plated layer is limited to 8-12 μm for the reasons as follows. The entire thickness of plated copper layer may be 15 μm and the thickness of the plated layer obtained by using a copper sulfate bath may be adjusted by varying the thickness of the plated layer obtained with the above-mentioned copper pyrophosphate plating bath.

The plated layer with the above-mentioned roughening treatment is further laminated with a plurality of layers of a composition prepared by infiltrating an insulating substance such as glass fibers with an epoxy resin, and then the aluminum foil pseudo-substrate is peeled off, thereby obtaining a final product.

In this case, the bonding strength between the plated copper layer subjected to the roughening treatment and said laminated insulating material may be about 1.6-1.8 kg/cm^2, but if it is less than 1.6 kg/cm^2, secondary roughening treatment copper plating is conducted on the outer side of the copper plated layer. For this purpose a method can be used in which, for example, cathodization is conducted at a current density of 2-20 A/dm^2 for 2-120 seconds in an acidic copper electrolytic bath having added therein ions of at least one metal selected from a group including arsenic, antimony, and bismuth.

Embodiments of the present invention will be described hereinbelow

Embodiment 1

A soft pure aluminum foil (99.9%) with a thickness of 70 μm was degreased by immersion for 3 min in a solution of sodium orthosilicate (100 g/L) at a temperature of 70°C, and then pickling and activation treatment was conducted by immersion for 1 min at a temperature of 25°C in an aqueous solution of HNO_3 with a concentration of 350 g/L. Then, an edge portion (edge width 20 mm) on only one side of the aluminum foil was selectively subjected to local zinc substitution plating by immersion for 60 sec in a solution (liquid temperature, room temperature) consisting of ZnO 30 g/L and NaOH 100 g/L. Then, one side of the aluminum foil was plated with copper for 5 min at an electric current density of 2 A/dm^2 in a plating bath (liquid temperature 50°C) having a Cu concentration of 30 g/L and a potassium pyrophosphate concentration of 150 g/L and a pH of 8.8. Finally, the plated layer was subjected to roughening copper plating for 2 min at a current density of 10 A/dm^2 in a plating bath (liquid temperature 20°C) containing Cu at 20 g/L and H_2SO_4 at 75 g/L. As a result, an ultrathin copper foil with a copper layer thickness of 6 μm was obtained.

Embodiment 2

A hard aluminum alloy foil (Al 99.7%, Cu 0.05%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 30 sec at a temperature of 50°C in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and nonionic surfactant 0.1 g/L. Then, pickling and activation treatment was conducted by immersion for 30 sec at a temperature of 25°C in a solution consisting of HCl 100 g/L and NaCl 50 g/L. Then, local zinc substitution plating was conducted selectively only on the edge portion (edge thickness 35 mm) on one side of the aluminum alloy foil by immersion for 38 sec in a solution (liquid temperature, room temperature) consisting of ZnO 5.0 g/L, NaOH 200 g/L, and $FeCl_3$ 5 g/L. One surface of the aluminum foil was then plated with copper for 10 min at a current density of 3 A/dm^2 in a plating bath (liquid temperature 60°C) consisting of Cu 80 g/L and potassium pyrophosphate 30 g/L, and having a pH of 9.3. Then roughening copper plating of said plating layer was conducted for 60 sec at a current density of 6 A/dm^2 in a plating bath (liquid temperature 25°C) consisting of Cu at 30 g/L and H_2SO_4 at 100 g/L. Finally, the resulting roughened plated layer was subjected to secondary roughening copper plating for 20 sec at a current density of 6 A/dm^2 in a solution consisting of Cu $(BF_4)_2$ 25 g/L, HBF_4 42 g/L, $Na_3AsO_412H_2O$ 0.9 g/L (liquid temperature 12°C), and an ultra thin copper foil with a copper layer thickness of 7 μm was obtained.

Embodiment 3

A hard aluminum alloy foil (Al 99.3%, Cu 0.04%, Fe 0.07%, Si 0.15%, Zn 0.05%, Mg 0.10%, Ti 0.05%) with a thickness of 50 μm was subjected to anodic electrolytic degreasing for 30 sec at a current density of 2 A/dm^2 in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and a nonionic surfactant 0.1 g/L. Then only the edge portion (edge width 15 mm) of the Al alloy foil was selectively subjected to local zinc substitution plating by treating for 20 sec in a solution (liquid temperature 30°C) consisting of ZnO 70 g/L and NaOH 400 g/L. Then, one surface of the aluminum foil was plated with copper for 15 minutes at a current density of 3 A/dm^2 in a plating bath (liquid temperature 60°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0. Then, the copper plated

layer was subjected to roughening copper plating for 75 sec at a current density of 32 A/dm^2 in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H_2SO_4 concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm^2 in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H_2SO_4 at 32 g/L, H_3AsO_4 at 0.4 g/L, and H_2SiO_3 at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 15 μm was obtained.

Comparative Example 1

A hard aluminum alloy foil (Al 99.7%, Cu 0.5%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 3 min in a solution (liquid temperature 70°C) consisting of sodium carbonate 30 g/L and sodium phosphate 50 g/L, and then an edge portion of 15 mm on one surface of the aluminum alloy foil was selectively subjected to zinc substitution plating by immersion for 20 sec in a solution containing ZnO at 70 g/L and NaOH at 400 g/L (liquid temperature 30°C). Then, copper plating was performed on the entirety of one surface of the aluminum alloy foil for 15 minutes at an electric current density of 3 A/dm^2 in a plating bath (liquid temperature 40°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0, then the copper plated layer was subjected to roughening copper plating for 75 sec at an electric current density of 32 A/dm^2 in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H_2SO_4 concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm^2 in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H_2SO_4 at 32 g/L, H_3AsO_4 at 0.4 g/L, and H_2SiO_3 at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 5 μm was obtained.

Comparative Example 2

An aluminum alloy foil identical to that of Comparative Example 1 was used and degreasing was conducted in the same manner as in Comparative Example 1. Then, copper plating similar to that of Comparative Example 1 was conducted immediately without zinc substitution plating and thereafter roughening copper plating was conducted to obtain an ultrathin copper foil with a copper layer thickness of 5 μm.

The ultrathin copper foils with pseudo-substrates attached thereto, which were obtained in the Embodiments 1-3 and Comparative Examples 1-2 were laminated on base materials infiltrated with glass epoxy and then pressing was conducted for 60 min at a pressure of 25 kg/cm^2 and a heating temperature of 160°C to obtain a laminated sheet with a thickness of 2 mm. Copper-clad laminated sheets were then obtained by mechanically peeling off the pseudo-substrates of aluminum foils, copper pyrophosphate plating was thereafter conducted to increase the thickness of the copper layer to 15 μm, and the bonding strength and pinholes were measured by the usual method. The results are presented in Table 1.

The bonding strength was measured by applying a peeling force in the direction of 90° to a width of 10 mm. The number of pinholes was counted by illuminating the layer from below a dark room and observing the transmitted light.

Table 1.

	Number of pinholes (holes/m^2)	Bonding strength (kg/cm^2)	External appearance of copper foil
Embodiment 1	2-4	1.6-1.7	Fine velvety peaks and valleys
Embodiment 2	1-2	2.0-2.4	"
Embodiment 3	0	20.-2.4	"
Comparative Example 1	20-100	1.5-1.7	Bulbous peaks and valleys
Comparative Example 2	Very large number	1.4-1.8	"

As follows from the table presented above, the ultrathin copper foils obtained by the method in accordance with the present invention have a number of pinholes substantially less than that in the ultrathin foils obtained by the conventional methods and also have excellent bonding strength.

Patent Representative. Patent Attorney: Takehiko Suzue.

5. List of Appended Items

(1) Power of attorney	2 copies
(2) Specification	1 copy
~~(3) Drawings~~	~~1 copy~~ 1 [illegible]
(3) ~~(4)~~ Copy of application	1 copy 3 [illegible]

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特許願(1)

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特許庁長官　斎藤英雄殿

1. 発明の名称

　極薄銅箔の製造方法

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明細書

1.発明の名称

　極薄銅箔の製造方法

2.特許請求の範囲

　アルミニウム箔又はアルミニウム合金箔の片面表面に亜鉛置換メッキを行つた後、該箔の全面にピロリン酸銅メッキ浴にて0.5〜12μの銅メッキを行い、更に片面の外側に硫酸酸性銅メッキ浴にて5〜12μの銅メッキを行うことを特徴とする極薄銅箔の製造方法。

3.発明の詳細な説明

　本発明は回路形成に際し回路を高密度に集積化した高密度プリント回路用極薄銅箔の製造方法に関するものである。

　近年電子技術の著しい発展に伴い、プリント回路板においては高密度にして高信頼性のものが要求されており、特に電子計算機のプリント回路用銅張積層板においては、回路密度増加に伴い線巾が0.2mm以下の如く微細な回路を形成しなければならない。然しながら従来使用されている銅箔は、その厚みが約35μの如く厚いため、通常のエッチング技術においては、その銅箔層を全部から回路を形成せしめる際、回路線がサイドエッチングによりアンダーカット状(回路の下側部分が局部的にエッチングされ、くぼみ状に侵蝕される状態をいう)となり断線するおそれがあるため、回路密度並に線巾間の高精度の回路を形成することができず、従つて高密度にして且つ高信頼性のプリント回路をうることができないものであつた。

　従つてこのような目的に適応する銅箔としては、18〜25μ程度の薄肉銅箔が使用されているが、この場合前記の薄肉銅箔の製造方法と現行の電解法により製造されているため、ピンホールが生成し易く、且つ薄肉のために取扱において、「しわ」「きず」等が発生し易い。又歩留も悪く、コスト高となるという欠点があつた。更にこのような銅箔をフォトレジスト法により回路配線を形成せしめる場合の回路線巾並に回路間隔は0.2mmが下限といわれ、それ以下の

細パターンを有する高密度配線の作成は困難であつた。

又この改良方法としてアルミニウム箔等を仮支持体とし、その上に電気メッキ法により厚さ10μ以下の銅箔の極薄メッキを形成せしめた複合体箔を使用し、銅箔面にガラスエポキシ基板等を積層した後、仮支持体のアルミニウム箔を化学的又は物理的の剥離方法により除去し、銅箔を導電体とし、これを前記のフォトレジスト法により高密度回路を形成せしめる方法が例えば特開昭48−83557号公報に記載されている。

然しながらこの方法は電気メッキにより形成される極薄銅箔と仮支持体のアルミニウム箔とを、よく密着せしめるために予め該アルミニウム箔の被電着面を亜鉛置換メッキしておく必要があると共にガラスエポキシ基材等を積層後、回路形成をするためには化学的にアルミニウムと亜鉛とを溶解除去しなければならない。従つてその工程が複雑であり且つ処理の制御が困難であると共に亜鉛を除去する際一部銅箔をも腐蝕され、断線割れを生じ易い欠点がある。

又他の方法として予め粗面、活性化した仮支持体のアルミニウム箔の片面上にシアン化銅メッキ浴により銅ストライクメッキを行うこともあるが、この結合力の密着性が十分でないため、その後の工程において、酸性銅メッキ浴により銅厚付メッキを行い、更に密着力の向上処理を行う際に、銅箔がアルミニウム箔表面から剥離し易く且つ銅ストライクメッキの厚さが12μ以下の場合には多数の微細なピンホールが存在し実用上使用し得ないものである。

本発明はかかる欠点を改善するため鋭意研究を行つた結果、極めて容易に、高密度のプリント配線を形成するための、極薄銅箔の製造方法を見出したものである。即ち本発明はアルミニウム箔又はアルミニウム合金箔（以下単にアルミニウム箔という）の片面縁部に亜鉛置換メッキを行つた後、該片面全面にピロリン酸銅メッキ浴にて0.5〜12μの銅メッキを行い、更にその外側に硫酸酸性銅メッキ浴にて8〜12μの銅メッキを行うものである。

本発明方法について以下詳細に説明する。

30〜70μのアルミニウム箔（巾300〜1300mmの長尺箔体）の少くとも片面を常法のアルカリクリーナー等により脱脂し水洗する。なおこの場合必要により50% HNO_3 等で酸洗もしくは活性化した後水洗する。

次いで該箔の片面の縁部を所謂ジンケート浴中に2〜120秒浸漬して、亜鉛置換メッキを施す。なおこの場合縁部とはアルミニウム箔の両縁に設けた帯状部分をいい、その巾は2〜100mm、望ましくは10〜50mmである。この巾を縁部巾という。

而して亜鉛置換メッキを施す理由は銅メッキされる部分のアルミニウム箔に対する銅箔の密着性を向上せしめるためである。即ちアルミニウム箔の縁部に亜鉛置換メッキを施さない場合にはピロリン酸銅メッキ自体アルミニウム箔面に対して十分な密着性を保持し得ないためであり、このような状態において水洗更には後工程における酸洗い等の前処理メッキを施す際に、アルミニウム箔の縁部から銅箔が剥離するのみならず一旦少しでも剥離すると急速に水又はメッキ液がアルミニウム箔と銅箔との界面に浸透し、銅メッキ液により主としてアルミニウム箔の表面を腐食しつつ一層剥離を助長する。このような状態のものを当然的には乾燥するとしても銅箔の大部分が仮支持体から剥離しているため「しわ」または無数のピンホールを生じ実用に供せないものとなる。しかし前記の如くアルミニウム箔の縁部に亜鉛置換メッキを施すことによりピロリン酸銅メッキ浴に対する密着性も良好であり且つその後の硫酸酸性銅メッキ浴中における剥離もおこらないと共に5μ以上の銅メッキを形成せしめた場合ピンホールは殆んど見られないものとなる。

而して亜鉛置換メッキを施した後直ちにピロリン酸銅メッキ浴により0.5〜12μの銅メッキを行い水洗する。この場合ピロリン酸銅メッキ浴の組成については特に限定するものではな

いが、好ましくは銅濃度5～100g/lピロリン酸カリウム100～500g/l、pH8～9.8のものがよい。又メッキ条件については液温を室温～70℃、電流密度1～5A/dm²、電解時間5～25分において行うものである。

又本発明においてピロリン酸銅メッキ浴を選んだ理由は他の銅メッキ浴に比してアルミニウム箔に対する密着性が比較的良好であり、プリント配線板用基材を積層せしめる際において自然に剥離のトラブルをおこすことがない。又に強固な密着性を保持し得ないことと相俟って、積層後、アルミニウム箔の全部分を化学的に溶解して除去する必要なく単に剥離剤の手にて剥離させることが出来るため溶液の処理も必要なく、単にアルミニウム箔としてそのまま回収することが出来る。更にピロリン酸銅メッキ層は電着を均一に行うことが出来るため、平滑にして光沢を有するメッキが可能であり、極薄銅箔とした場合においてもピンホールが極めて少い。又ピロリン酸銅メッキの厚さを0.5～12μに限定した理由は0.5μ未満の場合には得られた極薄銅箔はピンホールが多くなり実用上使用し難いものとなり、12μを越した場合には極薄銅箔としての厚さの上限が15μであるため、後工程の粗化処理銅メッキを行うことができなくなり且つプラスチックの積層素材との密着性に劣るためである。なお銅メッキ層の厚みは好ましくは3～7μが良い。

次いで上記銅層の上に凹凸化処理として硫酸酸性銅メッキ浴にて8～12μの銅メッキを施す。その条件については適宜選択すべきであり特に限定する必要はないが、一般的に硫酸メッキ浴の組成としては、銅濃度20～60g/l、硫酸濃度40～150g/l、浴温を常温～60℃にすることが望ましい。又電流密度並びに時間については液の流し方、攪拌状況、メッキ厚により一概にはいえないが通常5～40A/dm²、1～10分が好ましい。かくして得た銅メッキの外観は赤褐色のビロード状凹凸のものを形成することが必要である。

なお硫酸銅メッキ層の厚みを8～12μに限定した理由は全銅メッキ層の厚みが15μになればよく、前記のピロリン酸銅メッキ浴によるメッキ層の厚みの如何により、硫酸酸性銅メッキの厚みを調整すればよい。

次いで前記凹凸化せられたメッキ層の上に所望の積層物例えばガラス繊維にエポキシ樹脂を含浸したものを所定枚数積層した後、アルミニウム箔の積層体を剥離して製品化するものである。

なおこの場合凹凸化処理の銅メッキ層と積層物との剥離強さ力が1.6～1.8kg/cm²程度であればよいが、1.6kg/cm²未満の場合には、硫酸銅メッキ層の外側に2次凹凸化処理の銅メッキを行うものである。その方法としては例えばヒ素アンチモン、ビスマスの1種又は2種以上の金属イオンを0.0001～0.05mol/lを添加した硫酸銅浴中において電流密度2～50A/dm²、2～180秒間陰極処理を行うものである。

次に本発明の実施例について説明する。

実施例1

70μの軟質純アルミニウム箔(99.9%)をオルトケイ酸ナトリウム100g/lの溶液中に70℃において3分間浸漬して脱脂を行い、次いで350g/l HNO_3水溶液中に25℃において1分間浸漬して酸洗並活性化処理を行った後、該アルミニウム箔の片面端部(幅約20mm)のみを選択的にZnO 30g/l、NaOH 100g/lからなる溶液(常温、室温)中に60秒間浸漬せしめ部分亜鉛置換メッキを行った後、次いで該アルミニウム箔の片面をCu濃度30g/l、ピロリン酸カリウム150g/l、pH8.6からなるメッキ浴(液温50℃)中において電流密度2A/dm²により5分間銅メッキを行い、最後に該メッキ層をCu濃度20g/l、H_2SO_4 75g/lからなるメッキ浴(液温20℃)中において、電流密度10A/dm²により2分間凹凸化銅メッキを行って銅総厚6μの極薄銅箔を得た。

実施例2

30μ硬質アルミニウム合金箔(Al 99.7%、

Cu 0.05%, Fe 0.05%, Si 0.20%)をオルトケイ酸ナトリウム100g/ℓ, NaOH 30g/ℓ、ノニオン系界面活性剤0.1g/ℓからなる溶液中に50℃において30秒浸漬して脱脂を行い、次いでHCl 100g/ℓ, NaCl 50g/ℓからなる溶液中に25℃において30秒浸漬して酸洗並に活性化処理を行つた後、該アルミニウム合金箔の片面縁部(縁部巾35mm)のみを選択的にZnO 50g/ℓ, NaOH 200g/ℓ, $FeCl_3$ 5g/ℓからなる溶液(液温、室温)中に30秒間接触せしめ部分亜鉛置換メッキを行つた後、次いで該アルミニウム箔の片面をCu 80g/ℓ、ピロリン酸カリウム300g/ℓ, pH 8.3からなるメッキ浴(液温60℃)中において10分間、電流密度3A/dm²により銅メッキを行い、次いで該メッキ層をCu濃度30g/ℓ, H_2SO_4 100g/ℓからなるメッキ浴(液温25℃)中において60秒間、電流密度6A/dm²により凹凸化銅メッキを行い最後に該凹凸化メッキ層の上に$Cu(BF_4)_2$ 25g/ℓ, HBF_4 42g/ℓ, $Na_3AsO_4 \cdot 12H_2O$ 0.9g/ℓからなる溶液(液温12℃)中において20秒間、電流密度6A/dm²にて2次凹凸化銅メッキを行つて銅層厚7μの極薄銅箔を得た。

実施例3

50μの硬質アルミニウム合金箔(Al 99.3%, Cu 0.04%, Fe 0.07%, Si 0.15%, Zn 0.03%, Mg 0.10%, Ti 0.05%)をオルトケイ酸ナトリウム100g/ℓ, NaOH 30g/ℓ, ノニオン系界面活性剤0.1g/ℓからなる溶液中において30秒間電流密度2A/dm²により陰極電解脱脂を行い、次いで該Al合金箔の縁部(縁部巾15mm)のみを選択的にZnO 70g/ℓ, NaOH 400g/ℓから溶液(液温30℃)中に20秒間接触せしめて部分亜鉛置換メッキを行つた後、次いで該アルミニウム箔の片面をCu濃度100g/ℓ, ピロリン酸カリウム250g/ℓ, pH 9.0からなるメッキ浴(液温60℃)中において15分間、電流密度3A/dm²にて銅メッキを行い、次いで該銅メッキ層をCu濃度50g/ℓ, H_2SO_4 50g/ℓからなるメッキ浴(液温65℃)中において75秒間、電流密度32A/dm²にて凹凸化銅メッキを行い、最後に該凹凸化銅メッキ層の上にCu濃度7g/ℓ, H_2SO_4 32g/ℓ, H_3AsO_4 0.4g/ℓ, H_2SiO_3 0.2g/ℓからなる溶液(液温15℃)中において32秒間、電流密度4A/dm²にて2次凹凸化銅メッキを行つて銅層厚15μの極薄銅箔を得た。

比較例1

30μの軟質アルミニウム合金箔(Al 99.7%, Cu 0.5%, Fe 0.05%, Si 0.20%)を炭酸ソーダ30g/ℓ、リン酸ソーダ50g/ℓからなる溶液(液温70℃)中に3分間浸漬して脱脂を行い、次いで該アルミニウム合金箔の片面縁部15mmを選択的にZnO 70g/ℓ, NaOH 400g/ℓからなる溶液(液温30℃)中に20秒間浸漬して亜鉛置換メッキを行い、次いで該アルミニウム合金箔の片面の全面にCu濃度100g/ℓ, ピロリン酸カリウム250g/ℓ, pH 9.0からなるメッキ浴(液温40℃)中に15分間、電流密度3A/dm²にて銅メッキを行い、次いで該メッキ層の上にCu濃度50g/ℓ, H_2SO_4 50g/ℓからなるメッキ浴(液温65℃)中において75秒間、電流密度32A/dm²にて凹凸化銅メッキを行い、最後に該凹凸化銅メッキ層の上にCu濃度7g/ℓ, H_2SO_4 32g/ℓ, H_3AsO_4 0.4g/ℓ, H_2SiO_3 0.2g/ℓからなる溶液(液温15℃)中において32秒間、電流密度4A/dm²にて2次凹凸化銅メッキを行つて銅層厚5μの極薄銅箔を得た。

比較例2

比較例1と同様のアルミニウム合金箔を使用し、比較例1と同様に脱脂処理を行つた後亜鉛置換メッキを行うことなく、直ちに比較例1と同様の銅メッキを行い更に凹凸化銅メッキを行つて銅層厚5μの極薄銅箔を得た。

而して上記実施例1〜3及び比較例1〜2により得た仮基体付極薄銅箔をガラスエポキシ含浸基材の上に重ねた後、加熱温度160℃、圧

力25Kg/cmにおいて60分間加圧して、厚さ2mmの積層板とした後、アルミニウム箔の仮支持体と機械的に引き剥して銅貼積層板とした後、銅層の厚さを15μにするため、更にピロリン酸銅メッキを行い、常法により剥離力並にピンホールを測定した。その結果は第1表に示す通りである。

なお、剥離力は10mm巾につき90°方向の引き剥し力によるものであり、ピンホールは暗所において下方から光をあてて透過する穴の数をカウントした。

第1表

	ピンホール数 (個/m²)	剥離力 (Kg/cm²)	銅箔の外観
実施例1	2～4	1.6～1.7	微細ビロード状凹凸
2	1～2	2.0～2.4	〃
3	0	2.0～2.4	〃
比較例1	20～100	1.5～1.7	ダンゴ状凹凸
2	無数	1.4～1.8	〃

上表より明かの如く本発明方法により得た極薄銅箔は従来方法により得た極薄銅箔に比してピンホールが著しく少く且つ剥離力において優れたものを得る顕著な効果を有する。

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5. 添付書類の目録

(1) 委任状　2通
(2) 明細書　1通
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